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ENVIRONMENTAL FATE OF WHITE PHOSPHORUS/FELT AND
RED PHOSPHORUS/BUTYL RUBBER MILITARY SCREENING SMOKES:
PHASE I - LITERATURE REVIEW

FINAL REPORT

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We recommend that screening studies be performed to estimate the important of processes for which no data were reported and to verify some of the reported physical properties that were either derived from correlation equations or extrapolated to environmental conditions.

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FOREWORD

In conducting the research described in this report, the investigator(s) adhered to the "Guide for the Care and Use of Laboratory Animals," prepared by the Committee on Care and Use of Laboratory Animals of the Institute of Laboratory Animal Resources, National Research Council (DHEW Publication No. (NIH) 78-23, Revised 1978).

EXECUTIVE SUMMARY

The objective of this phase of the project was to review the literature for data that can be used to estimate the persistence of white and red phosphorus and their combustion products in air, soil, and aquatic environments and to identify gaps in the literature where such data are lacking.

We received the literature through on-line data files, including National Technical Information Service (NTIS), Chemical Abstracts, MEDLINE, TOXLINE, and TOXBACK 74 and 65. We also reviewed final reports on relevant phosphorus-related contracts supported by the U.S. Army. Very few rate constants necessary for an environmental fate assessment have been reported. We conclude that oxidation will be an extremely important process for white and red phosphorus and that hydrolysis reactions will dominate the transformation of phosphorus oxides in the presence of moisture. The findings of this report are summarized in Table IV of the report.

We recommend that screening studies be performed to estimate the importance of processes for which no data were reported and to verify some of the reported physical properties that were either derived from correlation equations or extrapolated to environmental conditions.

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I. INTRODUCTION

Smokes and obscurants are widely used in military operations to protect potential targets and to conceal movement of personnel and materiel. Although smokes have been used for decades in actual battle-ground and training situations, the U.S. Army is presently concerned with the environmental hazards and health risks associated with their manufacture and deployment. The manufacture and deployment of smokes generate wastes and a multitude of combustion products that can potentially contaminate soil, air, and water environments in the vicinity of their use. An understanding of how smokes and smoke products persist in such environments is now considered an integral part of any risk or hazard assessment.

White and red phosphorus are principal constituents in the military's smoke and obscurant program. Upon combustion, these two chemicals produce similar transformation products that interact with air, soil, and water environments. This report, which constitutes Phase I of the project, is a review of the available literature in a search for data that are critical in estimating the environmental fate of white and red phosphorus and their principal combustion products. Where data are not available, recommendations are made for further study in Phase II of this project. Also reviewed in this report are production and deployment methods, sampling techniques, and analytical methods that are applicable to phosphorus and its transformation products.

II. PRODUCTION AND DEPLOYMENT

A. Production

White phosphorus-containing munitions are manufactured at Pine Bluff Arsenal (PBA) located in Pine Bluff, Arkansas. Molten white phosphorus under water is shipped by tank car to PBA, where it is held in storage tanks until required for shell-loading.

Shell-loading is performed by the dip-fill and dry-fill methods (Berkowitz et al., 1981). The dip-fill method, in which shell canisters containing felt wedges are passed through tubes of molten phosphorus under water, is being phased out in favor of the dry-fill method, in which molten phosphorus is added directly to the canister in an inert atmosphere. The latter method greatly reduces phosphorus wastes (phossey water) and subsequent environmental contamination.

The pollution abatement facilities at PBA were significantly modified in 1979 to include a phossey water-treatment facility, scrubber systems to remove P_2O_5 from stack gases, and a phosphorus slag-recovery system. These facilities should minimize environmental pollution resulting from the manufacture of white phosphorus-containing munitions. Past manufacturing practices, such as the land disposal of phosphorus wastes, still remain a potential problem--digging in the areas shows the presence of active phosphorus. At present, red phosphorus is produced in Great Britain; therefore, no production wastes are generated in the United States. It is received at PBA as a formulation containing 95% red phosphorus and 5% butyl rubber.

B. Deployment

Smokes have many uses in tactical military situations, and a number of different scenarios have been described by Berkowitz et al.

(1981). Our concern with deployment practices is the generation, size distribution, and behavior of smoke particles under various environmental conditions.

Katz et al. (1981) reported that in the combustion of white phosphorus/felt (WP/F) mixtures, mass median diameters (MMDs) of smoke particles ranged from 0.3 to 1.2 μm at relative humidity ranging from 5 to 75%. However, there was no clear relationship between particle size and relative humidity. The smoke generated approximately 1000 particles/ cm^3 and the total mass concentration of smoke was near 150 $\mu\text{g}/\text{m}^3$.

Ballou (1981) generated smoke from red phosphorus/butyl rubber (RP/BR) and reported MMDs between 0.9 and 1.4 μm at relative humidity of 20 to 50%. The particle sizes were said to be in good agreement with those found in previous investigations (Weimar et al., 1977; Milham et al., 1977; Carlson et al., 1977). Mass concentrations given by Ballou et al. (1981) ranged from 2 to 10 g/m^3 and were considered to be quite high. Nevertheless, this result suggests that the method of deployment can significantly affect the total smoke concentration. However, none of the above investigators reported rate constants for the deposition of particles on environmental surfaces (deposition velocity).

III. SAMPLING TECHNIQUES

The sampling of smoke vapors and particles for chemical identification is a difficult task because of the reactive nature of phosphorus transformation products to oxygen and water, which are also present in the smoke-generation atmosphere. Ballou et al. (1981) used glass-fiber filters and water-filled impinger tubes to collect phosphorus oxides and found that hydrolysis reactions occurred readily; in particular, they occurred more rapidly on glass-fiber filters than in the water impingers.

Katz et al. (1981) used glass wool as a collection device for smoke particulates and extracted trapped species from the wool with methanol. Impinger solutions of deoxygenated xylene were also used to trap phosphorus volatiles such as P_4 . In later studies, the trapping system was modified by passing gases through three liquid oxygen cold traps, where long-chained (P_2 to P_8) polyphosphoric acid moieties were trapped. However, Ballou and Katz gave little information regarding trapping efficiency or stability of the compounds in the trapping medium.

Several methods for collection of phosphine have been reported in the literature. Destructive sorbents such as silica gel impregnated with silver nitrate and potassium permanganate (Greifer et al., 1974) have been used in the collection and conversion of phosphine for colorimetric determination. Phosphine reduces silver nitrate to metallic silver, leaving a black stain. Potassium permanganate and silica gel impregnated with potassium permanganate oxidize the phosphine to phosphate for subsequent colorimetric determination as a phosphomolybdate complex. Potassium permanganate alone was a good sorbent, but oxidation did not proceed due to lack of moisture. Potassium permanganate impregnated on silica gel contained the

necessary moisture for oxidation to proceed; however, interferences from the potassium permanganate and silica gel precluded a colorimetric determination (Taylor, 1975).

Muthu et al. (1973) reported collection of phosphine on paper-strip detectors dipped into a 1% solution of mercuric chloride in methyl yellow. The release of HCl in the formation of $P(HgCl)_3$ causes the color to change from yellow to red. Kobayashi and Meguro et al. (1967) detected phosphine by collecting it on silica gel impregnated with $AuCl_3$ and noting the resultant color change. Silica gel and activated charcoal have been used to nondestructively collect phosphine (Greifer et al., 1974; Bochkarev and Khripunov, 1963). Greifer et al. (1974) reported that silica gel was not suitable because of its low capacity for phosphine.

From the above reports, it appears that cryogenic trapping may serve as the best sampling approach until better approaches are found.

IV. ANALYTICAL METHODS

A. General

The separation and quantitation of phosphorus oxyacids are described in several excellent books (Van Wazer, 1958; Halmann, 1972). Methods from these sources and from the open literature are described in this section.

Most methods of analysis for phosphorus compounds involve conversion to orthophosphate and analysis by one of several possible analytical methods--most commonly, colorimetry of a phosphate complex (Murphy and Riley, 1958). Other methods of analysis based on orthophosphate complex formation are fluorimetry (Guyon and Shults, 1969; Holzbecher and Ryan, 1973) and a radioactive tracer technique (Hahn and Schmitt, 1969). Colorimetry is time-consuming and subject to a number of interferences. Fluorimetry has the advantage of greater sensitivity and less error from interferences; however, it is an indirect measure of orthophosphate and is time-consuming. The radioactive tracer technique is very sensitive but requires equipment not found in most laboratories.

Orthophosphate can be determined by electrochemical and colorimetric titration of the excess metal used to precipitate it (Tutundzic and Stojkovic, 1966; Pehler, 1967). These methods measure orthophosphate indirectly and are subject to a number of interferences; furthermore, the colorimetric titration is a lengthy operation.

The development of an inductively coupled plasma excitation source, which is used with optical emission spectroscopy, has resulted in a sensitive method of analysis for phosphorus and other elements (Fassel and Kniseley, 1974). This method is a recent development and is not available commercially. Construction of an instrument would be

necessary for this approach. Neutron activation and atomic absorption spectrophotometry have also been used for analysis of phosphorus-containing materials. Neutron activation analysis is very sensitive but it is costly, requiring equipment not found in most analytical laboratories. Atomic absorption spectrophotometry methods for analysis of phosphorus are indirect and are not as sensitive as the inductively coupled plasma-optical emission spectroscopy method.

Potentiometric titration has been employed by Wolfe and Jung (1931), Burton et al. (1982), and Ballou (1981) in the assay of mixtures of the lower oxyacids or phosphorus. This approach is based on the fact that most oxyacids are strong acids. Burton and Ballou found that in spite of the presence of several phosphorus oxyacids in a mixture, the total phosphorus concentration could be determined by simple titration. This is possible because there is precisely one strongly acidic hydrogen for each phosphorus atom in all the lower linear and cyclic phosphorus oxyacids.

B. Paper Chromatography

Thakur (1970) used paper chromatography, with tri-n-butyl orthophosphate as an eluting solvent, to separate $P_2O_7^{4-}$, PO_4^{3-} and PO_3^{3-} .

Karl-Kroupa (1956) described a quantitative method, using paper chromatography, for separating mixtures containing ortho-, pyro-, and triphosphates (tripolyphosphates) as well as rings (trimeta- plus tetrametaphosphates) and long-chain phosphates. This technique involved a two-dimensional chromatogram in which the first and second solvents advanced in opposite directions (180° apart).

C. Thin-Layer Chromatography

Burns and Lee (1969) used thin-layer chromatography to separate HPO_4^{2-} , $P_2O_7^{2-}$, $P_3O_{10}^{5-}$, PO_3^{2-} , $H_2PO_2^{2-}$, HPO_3^{2-} , $HP_2O_6^{3-}$, and several meta- and poly phosphates. Two separations were necessary to resolve the above phosphorous anions—one using an acidic eluting solvent and the other using a basic eluting solvent. The plates were developed by

spraying with a molybdate solution followed by ultraviolet (UV) irradiation.

D. Open-Column Chromatography

Several methods using open-column chromatography can be used to separate oxy anions of phosphorus. Ohashi et al. (1970) used ion exchange to separate linear polyphosphates. Gradient elution techniques were necessary to obtain separation of P_{18} linear polyphosphates. Similarly, Rothbart et al. (1964) used ion exchange chromatography to separate orthophosphate, linear polyphosphates, and three cyclic polyphosphates. One eluent separated the low-polymeric phosphates; then another eluent was used to elute the high-polymeric phosphates. Both Ohashi and Rothbart used colorimetry for detection of the phosphates. Another open-column technique used to separate the oxy anions of phosphorus was gel chromatography, which separates on the basis of molecular size. Ohashi et al. (1970) used this technique to separate orthophosphate, diphosphate, triphosphate, and Kurrol's salt.

E. Ion Chromatography

Ion chromatography developed by Small et al. (1975) is a unique adaption of high-performance liquid chromatography (HPLC)/ion exchange chromatography. For the analysis of anions, such as the oxy anions of phosphorous, weak acid anions (i.e., carbonate, bicarbonate, etc.) are used as counter ions to separate the sample anions on an anion exchange column. The effluent from the anion exchange column is passed through a suppressor column (a cation exchange column in the acid form), which converts the weak acid eluent anions to the unionized acid. The sample anions pass through the suppressor column but remain ionized because their pK_a is higher than that of the eluent anions. The sample anions are then detected by a conductivity detector. Anions should have a $pK_a > 7$ in order to be analyzed by this method.

HPLC with an ion exchange column has been used by Yamaguchi et al. (1979) to separate linear and cyclic condensed phosphates. The HPLC was interfaced with an automatic phosphate analyzer (colorimetric) for detection of the phosphates. Gradient elution was necessary to achieve the separation of more than 30 kinds of condensed phosphates.

An HPLC flow-injection system was developed by Hirai et al. (1981) for the rapid flow analysis of lower oxyacids of phosphorus such as phosphinate and phosphonate. Lower oxyacids of phosphorus could be determined at a sampling rate of 60 samples per hour with a relative standard deviation of less than 1%.

F. Gas Chromatography

Direct gas chromatography of phosphorus and phosphine has been reported (Burchfield and Wheeler, 1966). This approach is direct and simple. Conditions for the gas chromatography of phosphorus and phosphine, including temperature and chromatographic columns, are similar, which should enable the simultaneous analysis of these two substances if a sorbent that will collect both can be found. A variety of detectors have been used for the detection of phosphorus and phosphine. They include a thermal conductivity detector (TCD) (Muthu et al., 1973), a thermionic detector (TID) (Bochkarev and Khripunov, 1963), a flame photometric detector (FPD) (Bochkarev and Khripunov, 1963; Burchfield and Wheeler, 1966; Butts and Rainey, 1971; Weise and Hanson, 1972), and an electron-capture detector (ECD) (Chakrabarti and Waiman, 1972). If phosphorus is pyrolytically reduced with hydrogen, a microcoulometric detector (MCD) can be used to detect phosphine and phosphorus (as phosphine) (Bochkarev and Khripunov, 1963). In sensitivity, selectivity, and simplicity, the FPD is considered superior to the rest of the detectors.

G. ^{31}P Nuclear Magnetic Resonance

Data on ^{31}P chemical shifts have been published for thousands of phosphorus compounds, including the oxyacids. Among the first workers to realize the power of nuclear magnetic resonance (NMR) for the detection of these acids were Van Wazer et al. (1958) and Callis et al. (1956), who published data on the chemical shift of phosphate, hypophosphite, and pyrophosphite anions. Later, Crutchfield et al. (1962) reported ^{31}P chemical shifts for ortho-, pyro-, tripoly-, tetrapoly-, trimeta-, and tetrameta-phosphate in concentrated aqueous solutions over the pH range of 0 to 12. Moedritzer (1967) found that the ^{31}P chemical shifts of a series of oxyacids of phosphorus varied linearly with the degree of neutralization.

Included in a text on ^{31}P NMR (Grayson and Griffith, 1967) is a compilation of chemical shifts for over 3,000 phosphorus compounds. The data in Table 1 demonstrate the wide range of chemical shifts reported in that text for elemental phosphorus, phosphorus oxides, phosphorus oxyacids, and phosphine.

Table 1

CHEMICAL SHIFTS FOR PHOSPHORUS SPECIES

<u>SPECIES</u>	<u>(PPM)</u>
Phosphorus trioxide	-113
Hypophosphorus acid	-12.0
Phosphorus acid	-4.5
Diphosphorus acid	-1.7
Orthophosphorous acid	0
Pyrophosphoric acid	+10.6
Tripolyphosphoric acid	+11.5
Tetrapolyphosphoric acid	+20.7
Cyclotriphosphoric acid	+24.0
Phosphine	+238
Phosphorus (elemental, white)	+460

V. ENVIRONMENTAL FATE

To assess the persistence of phosphorus and its combustion and transformation products in the environment, reliable data must be available to provide estimates of movement (transport) and loss (transformation) of species generated in the manufacturing and deployment practices. Based on the studies of Katz et al. (1981), Ballou (1981), Sullivan et al. (1979), and Lai and Rosenblatt (1977), the compounds listed in Table 2 have been identified as smoke components of environmental concern. Table 2 also shows various physical properties and transport and transformation processes for which data must be assembled to arrive at an environmental assessment. A number of processes can be estimated to be insignificant, such as the biotransformation of phosphorus pentoxide (P_4O_{10}), because hydrolysis reactions are expected to be dominant in the aquatic and soil environments. The importance of other processes cannot be assessed until the magnitude of the rate constant is known for the competitive processes, thereby enabling an estimation to be made as to the significance or insignificance of a specific process. The following sections review the available literature in the areas of physical transport, chemical transformation, and biotransformation.

Table 2

CHEMICALS DERIVED FROM THE MANUFACTURE AND DEPLOYMENT OF
PHOSPHORUS MUNITIONS AND PROPERTIES AND PROCESSES THAT NEED TO
BE EVALUATED FOR A FATE ASSESSMENT

Chemicals	Properties and Processes
White phosphorus	Solubility
Red phosphorus	Vapor pressure
Phosphorus pentoxide, P_4O_{10}	Evaporation rate from soil and water
Phosphorus trioxide, P_4O_6	Sorption partition coefficient, K_p/K_{oc}
Hypophosphorus acid, H_3PO_2	Octanol/water partition coefficient, K_{ow}
Phosphorus acid, H_3PO_3	Leachability
Polyphosphoric acids, P_2-P_8	Henry's constant, H
Cyclic metaphosphates, P_3, P_4, P_6	Particle deposition rate
Phosphine, PH_3	Dissolution rate
Phosphoric acid, H_3PO_4	Diffusion rate
	Hydrolysis rate--air, soil, water
	Oxidation rate--air, soil, water
	Reduction rate--air, soil, water
	Absorption spectrum
	Photolysis rate--air, soil, water
	Quantum yield
	Biotransformation rate--aerobic, anaerobic
	Biosorption partition coefficient, K_B
	Biouptake
	Bioaccumulation

A. Physical Transport Properties

1. Water Solubility

The water solubility of white phosphorus is given in the 45th edition of Handbook of Chemistry and Physics (Weast et al., 1964-1965) as 3 mg L^{-1} at 15°C . Lai and Rosenblatt (1977) reported that the solubility of white phosphorus in water appears to be a function of the concentration of dissolved oxygen. Indeed, their data suggest that much of the white phosphorus in phosphy water is colloidal rather than dissolved, and that this colloid/solution mixture of elemental phosphorus reacts with dissolved oxygen and hydroxide ions to form phosphine and phosphorus oxides and acids. Thus, it is clear that the measurement of the solubility of white phosphorus must be undertaken with care to minimize or account for the presence of colloidal particles and for the reactivity of dissolved species with oxygen.

The solubility of red phosphorus was not quantitatively given in the literature. Berkowitz et al. (1981) alleged that red phosphorus was very slightly soluble in water (presumably less soluble than white phosphorus), but gave no quantitative data. They stated that red phosphorus is less reactive than white phosphorus but, clearly, precautions in minimizing the reactivity of red phosphorus should be taken when measuring its aqueous solubility.

The solubilities of P_4O_{10} and P_4O_6 are not important because of the fast hydrolysis of these compounds. Hypophosphorus acid (H_3PO_2) and phosphorus acid (H_3PO_3) are, of course, completely soluble in water. No data were found on the solubilities of the polyphosphoric acids (P_2 - P_8) or the cyclic (P_2 , P_4 , P_6) metaphosphates, but these acids are expected to be completely soluble in water.

Berkowitz et al. (1981) list phosphine as being sparingly soluble. It is unlikely that phosphine would persist very long in water because of its very high vapor pressure at environmental temperatures and its reactivity with dissolved oxygen. Therefore, mea-

surement of the aqueous solubility of phosphine is not critical to environmental fate assessment.

2. Octanol/Water Partition Coefficient

No octanol/water partition coefficients were found for any of the chemicals listed in Table 2. The octanol/water partition coefficient (K_{ow}) may be estimated, however, from the water solubility of the chemical by using a simple correlation equation (1) developed by Yalkowsky and Valvani (1980):

$$\log K_{ow} = -\log X_s - 1.04 - \frac{\Delta H_f}{T_m (1360)} (T_m - T)/1.08 \quad (1)$$

where X_s is the mole fraction solubility, ΔH is the enthalpy of fusion, T_m is the melting point of the solute, and T is the temperature of interest. For white phosphorus, using data compiled by Berkowitz et al. (1981), a value of 4.9 is calculated for $\log K_{ow}$ at 288.2°K (15°C). The K_{ow} can also be estimated using the correlation equation described by Karickhoff et al. (1979), from which a $\log K_{ow}$ of 4.2 is derived.

It should be noted that equation (1) was derived for nonpolar organic chemicals. Because of the importance of K_{ow} in environmental assessments and the relative ease of measurement, K_{ow} values should be measured for white and red phosphorus. K_{ow} values for any of the other phosphorus compounds listed in Table 2 may be insignificant because these compounds hydrolyze quickly or ionize in water.

3. Vapor Pressure

The vapor pressures for white and red phosphorus were obtained from the 54th edition of Handbook of Chemistry and Physics (Weast et al., 1973-1974). The data (Table 3) are given in terms of the Clapeyron equation (2):

$$\log_{10} P(\text{torr}) = (-0.2185 A/T) + B \quad (2)$$

where T is in degrees Kelvin, A is a function of enthalpy, and B is a constant.

Table 3

PARAMETERS FOR CALCULATING THE VAPOR
PRESSURE OF PHOSPHORUS

	<u>A</u>	<u>B</u>	<u>Range (°C)</u>	<u>P (torr)</u>
White phosphorus	15090	9.6511	20.0 to 44.1	0.04 (at 25°C)
	12530	7.8233	76.6 to 280	1 (at 76.6°C)
Red phosphorus	25950	11.1130	237 to 417	---

Thus, the calculated vapor pressure for white phosphorus is 0.04 torr at 25°C and 1 torr at 76.6°C; for red phosphorus it is 1 torr at 237°C. We are not aware of the source of the CRC data. Berkowitz et al. (1981) also list a vapor pressure of 1 torr at 76.6°C for white phosphorus, without reference. Because of the difficulty of measuring vapor pressures at 1 torr and lower (particularly for reactive chemicals) and because of the inaccuracy of using the Clapeyron equation to extrapolate data in this vapor pressure range, it is important that the vapor pressures of white and red phosphorus be measured.

The vapor pressure of phosphine was estimated from the boiling point, critical pressure, and critical temperature of phosphine, using the following equation (3) taken from Reid et al. (1977):

$$\ln P_r = T_{br} \left(\frac{\ln P_c}{1 - T_{br}} \right) \left(1 - \frac{1}{T_r} \right) \quad (3)$$

where P_r is the reduced pressure at temperature T , T_{br} is the reduced boiling temperature, P_c is the critical pressure, and T_r is the reduced temperature. At 20°C the pressure is calculated to be 36 atmospheres; therefore, phosphine is expected to rapidly partition into the gas phase in the environment.

The vapor pressures of P_4O_{10} , P_4O_6 , and the acids listed in Table 2 are not needed for environmental fate assessment. P_4O_{10} and P_4O_6 are not expected to persist in the environment because of their reactivity. Moreover, the Henry's constants of the acids are more relevant to their environmental fate than vapor pressures; consequently, we will focus our attention on this property.

4. Henry's Constant/Volatilization from Water

The screening study for volatilization from water consists of estimating or measuring the value of H for the solute. Henry's constant is defined by equation (4):

$$P = HC \quad (4)$$

where C is the concentration of the chemical in water. For solutes with low solubility, H can be estimated from the vapor pressure of the pure solute, P_g (saturated vapor pressure), and the aqueous solubility of the solute (S):

$$H = P_g / S \quad (5)$$

Thus, a value of $H = 400$ torr liter mole⁻¹ is calculated from the solubility and extrapolated vapor pressure of white phosphorus at 15°C. White phosphorus would appear to have intermediate volatility and its volatilization rate would depend on both liquid- and gas-phase mass transport resistance.

Phosphine has very high vapor pressure at ambient temperature and is sparingly soluble in water. Thus, the Henry's constant for phosphine is high and its water volatilization will be high and will depend on the turbulence of the water phase. Lai and Rosenblatt (1977) measured a loss of 80% to 90% of total phosphine from water within two days (the conditions were not specified). This result confirms the expectation that volatilization will be an important transport process for phosphine.

5. Volatilization from Soil

We are unaware of any measurement of the volatilization from soil of any chemicals listed in Table 2.

In general, mass transfer of a soil-incorporated chemical to the soil-atmosphere boundary layer depends on the rate of diffusion of the chemical in the soil-air and/or movement of the chemical with bulk water flowing to the surface by capillary action during water evaporation (wick effect). In general, soil-air diffusion is most important for chemicals with intermediate to high Henry's constants (between 100 and 3500 torr liter mole⁻¹), and wicking is important for chemicals with low values of H (< 100 torr liter mole⁻¹) in wet soils during drying periods.

However, we do not expect that diffusion of chemical vapors in the soil-air will be an important environmental process for most of the chemicals (except for phosphine and possibly red phosphorus) listed in Table 2. White phosphorus would appear to have intermediate volatility; however, it would probably be oxidized rapidly to oxyacids in unsaturated soils relative to the rate of soil-air diffusion. The acids listed in Table 2 are expected to have low H values and therefore should partition primarily in the soil-water phase.

The soil-air diffusion of phosphine should be rapid because of its high H value and its low molecular weight; therefore, phosphine is not expected to persist in unsaturated soils. The value for red phosphorus and its oxidation rate in air will have to be known before

the possible significance of soil-air diffusion of red phosphorus vapor can be determined.

Wicking should be an important soil-transport mechanism for the acids listed in Table 2. The flux of chemicals to the soil surface by wicking is expressed by $F_w C_L$, where F_w is the water flux ($\text{cm}^3 \text{cm}^{-2} \text{hr}^{-1}$) and C_L is the concentration of the chemical in the soil-water phase. If the H value for a chemical is very low, C_L can be calculated from equation (6):

$$C_L = \frac{\theta_w C_T}{\theta_w + \theta_s K_p d} \quad (6)$$

where C_T is the total amount of chemical per unit volume of soil, θ_w and θ_s are the volume fractions of soil-water and soil-solid, K_p is the sorption partition coefficient, and d is the bulk density of the soil. Therefore, the flux of chemicals to the soil surface can be determined by the soil-water evaporation rate, F_w , K_p , and d , if the water content and the overall chemical loading in the soil are known. Once the chemical reaches the soil surface, the volatilization rate will be determined by Henry's constant and the turbulence of the atmosphere boundary layer.

6. Sorption Partition Coefficient

The adsorption of phosphates in soil-water systems was recently reviewed by Berkheiser et al. (1982). Phosphate adsorption isotherms are commonly fitted to the Langmuir model. These isotherms are non-linear, with the sorption partition coefficient being a function of the concentration C , as shown in equation (7):

$$K_p = \frac{b S_{\max}}{1 + bC} \quad (7)$$

where b is a constant and S_{\max} is the limiting amount adsorbed. At sufficiently dilute concentrations, the isotherm is linear and K_p is

given by $b S_{\max}$. Based on a limited amount of data, K_p for phosphate adsorption was found to be significantly correlated with oxalate-extractable Fe and Al. However, a universal predictive equation based on active Fe and Al content, similar to that using the organic carbon content to predict sorption of nonpolar organics on soils, has not been developed.

Berkheiser et al., (1982) also note that phosphate adsorption involves two steps; the first is complete within a few hours and the second may continue for weeks or months. Temperature and pH also significantly affect the extent and rate of adsorption.

Edzwald (1977) recently reviewed the adsorption of phosphates on sediments. Phosphate adsorption on sediments also depends on the concentration of oxalate-extractable Fe and Al. Indeed, it would appear that phosphate adsorption mechanisms are similar on soils and sediments.

The adsorption of nonpolar white phosphorus or red phosphorus from water on soils or sediments is expected to be significantly different from the adsorption of phosphate ions. From data reported by Lai (1981), a sorption partition coefficient of 77 ± 12 can be determined although the soil was not well characterized. It may be possible to correlate red or white phosphorus adsorption on soils or sediments with the fractional organic carbon content. The sorption partition coefficient normalized for organic carbon content ($K_{oc} = K_p/F_{oc}$) may be estimated from the aqueous solubility, using a correlation equation suggested by Karickhoff et al. (1979):

$$\log K_{oc} = -0.54 \log S_w + 4.31 \quad (8)$$

where S_w is the aqueous solubility in ppm. For white phosphorus, the calculated value for $\log K_{oc}$ is 4.05 at 15°C. If equation (8) is valid for white phosphorus the organic fractional content of the soil used by Lai (1981) is 0.68% carbon. The aqueous solubility of red

phosphorus is not known and hence its sorption coefficients cannot yet be estimated.

7. Leachability

The composition of a leachate of a soil contaminated with phosphorus smoke production and/or combustion wastes will depend, in a very complex manner, on chemical transformations in the soil matrix, partitioning of the phosphorus chemicals between the soil-air, soil-water and soil-solid phases, and the rates of adsorption and desorption relative to the rate of water flow.

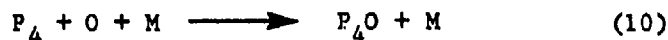
Leaching of phosphates has been studied by Berkheiser et al. (1982). However, no data are available on the leachability of the lower oxides of phosphorus, elemental phosphorus, or phosphine.

B. Chemical Transformation

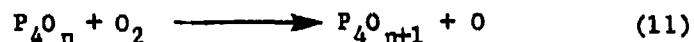
1. White Phosphorus

a. Oxidation

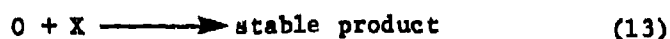
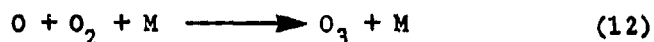
Vapor phase. The dominant chemical transformation for white phosphorus in munition smokes is oxidation. The oxidation of phosphorus vapor has been extensively studied (Van Wazer, 1958). The reaction is thought to proceed by a branching-chain mechanism. According to this theory, each reactant has upper and lower critical pressures. The reaction is very rapid between these limits and very slow outside of them. The chain part of this mechanism consists of the following steps:



where M is another atom and may not be necessary,



where n = 1 through 9,



where X is a "poison" to the reaction (for example, the wall of the reaction vessel). It has been reported that reaction (9) has no activation energy (Dainton and Kimberly, 1950). Thus, the rate of the reaction is diffusion-limited.

However, it is doubtful that phosphorus vapor is a component of these smokes because its vapor pressure is only 0.072 mm Hg at its auto-ignition temperature (30°C). The oxidation is expected to be more rapid than vaporization. It has been reported that when these phosphorus munitions are deployed, white phosphorus particles settle to the ground and continue burning for 6-7 minutes (Berkowitz, et al. 1981). This is the only available information on the practical oxidation rate of these munitions.

Aqueous phase. White phosphorus in wastewaters exists in three forms: dissolved phosphorus (3 mg/L), colloidal white phosphorus, and larger, suspended white phosphorus particles. The rate of oxidation of this physical mixture is dependent on the interconversion of the forms. Sullivan et al, (1979) reviewed the reported rates of oxidation of P_4 in water. The reported rates depend on pH, dissolved oxygen content, temperature, and metal ion concentration. Reported half-lives for dissolved P_4 range from 0.85 to 20 hr. For mixtures

containing colloidal and particulate white phosphorus, a half life as high as 300 hr has been reported (Zitko, et al. 1970).

Dissolved white phosphorus initially decomposes via a first-order reaction. Earlier studies reported that this first-order reaction proceeds until the WP concentration falls to below 0.01 ppm, with decomposition being slower thereafter until equilibrium levels of 0.04 to 0.10 ppb are reached. Preliminary results reported by Sullivan et al. (1979) suggest that dissolved WP decomposes to below 0.01 ppb rapidly; no observation was made regarding any inflection in the decomposition rate. The suggestion was presented that the earlier results were due to an analytical problem.

The kinetics of this oxidation are strongly dependent on oxygen concentration. It has been suggested that the kinetics in water may parallel the kinetics of the vapor-phase reaction. By this theory, there should be minimum and maximum critical concentrations of oxygen between which the reaction is very rapid and outside of which the reaction is much slower. The theory has yet to be well tested for aqueous systems. Since the oxygen concentration in phossey water has been reported to be significantly lowered (Lai and Rosenblatt, 1977), this mechanism would result in a significantly longer lifetime of P_4 in the environment.

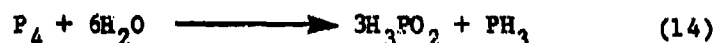
It has also been reported that metal ions have a strong effect on the oxidation rate. Copper ions were reported to increase the oxidation rate by an order of magnitude, and iron ions decrease the rate by a similar factor (Sullivan, 1979). Because of the presence of metal ions in natural waters, this effect should be studied in greater detail.

Solid phase. The oxidation of solid white P_4 has been extensively studied (Van Wazer, 1958). The mechanism has been shown to involve a branching-chain mechanism similar to that described for vapor-phase oxidation. As in vapor-phase oxidation, there are upper and lower critical oxygen pressures. At atmospheric pressure in air

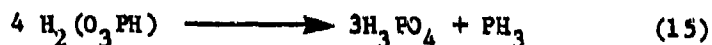
and 30°C we are near the upper limit for combustion; only a slow reaction is expected in this region. However, this slow reaction is exothermic and the temperature rises until the upper limit of oxygen pressure is above the oxygen pressure and combustion results. The rate of combustion is essentially diffusion-controlled. However, in soils or sediments where the partial pressure of oxygen is low, the lifetime of white phosphorus would be long.

b. Hydrolysis

White phosphorus reacts with water according to equation (14):



According to Lai and Rosenblatt (1977), this reaction amounts to between 6 and 9% of the total reacted WP. Thus, the rate of this hydrolysis must be competitive with the rate of oxidation. First-order hydrolysis rate constants of 7×10^{-3} to $7 \times 10^{-2} \text{hr}^{-1}$ are calculated from the reported oxidation rates. This must be considered an upper limit because they determined this number by detecting PH_3 produced, which can also result from reaction (15):



The hydrolysis is strongly pH-dependent. The gas-phase hydrolysis of P_4 has been reported to be catalyzed by metal ions and by H_3PO_4 (Van Wazer, 1958).

c. Photochemistry

No data on the UV-VIS spectra or photochemistry of white phosphorus in water have been reported. However, the photochemical initiation of conversion of white phosphorus to red phosphorus has been reported in PBr_3 and CS_2 solutions. Once initiated, this reaction has been reported to proceed with a rate constant of $7.8 \times 10^{-3} \text{min}^{-1}$ at

184°C. This will be used as an upper limit in water (Van Wazer, 1958).

Solid white phosphorus has been reported to be photochemically converted to red phosphorus (Van Wazer, 1958). The rate constant (or quantum yield) must be small because only small amounts of red phosphorus are found on the surface of white phosphorus after exposure to UV light "for a considerable length of time." No quantitative data were reported.

d. Reduction

Reduction is not considered to be an important fate process for white phosphorus. Reduction products do result from oxidative disproportionation reactions (equation 14) that were covered in the hydrolysis section.

2. Red Phosphorus

The vapor pressure and solubility of red phosphorus are extremely small. Therefore, solution and vapor-phase chemistry are probably negligible.

In the solid state, red phosphorus reacts with water vapor and oxygen to form phosphine and a mixture of oxyacids. At normal temperatures and humidities, this reaction is slow (Van Wazer, 1958). However, this reaction can be catalyzed by metal ions. Iron and copper, which are present in commercial red phosphorus, markedly increase the oxidation rate. Red phosphorus burns in air above 260°C and the combustion products are similar to those for white phosphorus.

3. Phosphorus Oxides

a. Phosphorus Pentoxide (P_4O_{10})

Phosphorus pentoxide is the major product when white or red phosphorus is combusted in an excess of air; P_4O_{10} can not be further

oxidized. The major environmental chemical transformation is by hydrolysis. The sublimation temperature of 360°C may lead to some volatile P_4O_{10} being present in the phosphorus munition smokes. In any case, both the vapor-phase and solid-phase hydrolysis reactions are diffusion-limited. The hydrolysis mechanism is discussed by Osterheld (1972). The products of hydrolysis of P_4O_{10} are primarily tetrameta-phosphoric acid (77%), tripolyphosphoric acid (15%), and a mixture of trimeta-, tetrapoly-, and orthophosphoric acids. Reaction with alcohols results in organophosphates.

b. Phosphorus Tetroxide (P_4O_8)

When phosphorus burns in a limited supply of air at moderately high temperatures, this oxide is formed as part of the resulting mixture of oxides. Very little is known about its chemical properties. Hydrolysis and oxidation are both expected. No kinetic data are available.

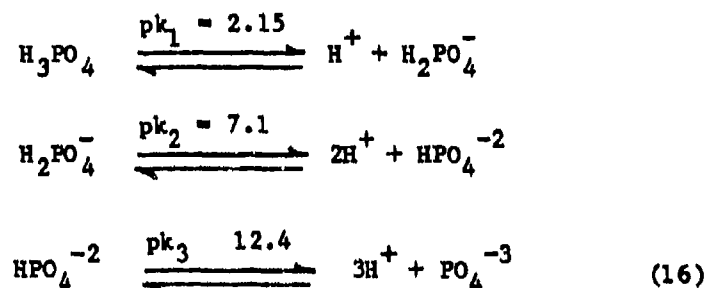
c. Phosphorus Trioxide (P_4O_6)

Phosphorus trioxide is formed when phosphorus is burned in an oxygen-deficient atmosphere. It is thermally unstable above 210°, decomposing into red phosphorus and other PO_x oxides. It is stable to oxygen at room temperature. At low temperatures it reacts with water to give phosphorus acid. At higher temperatures this reaction is more complicated, producing phosphine, phosphoric acid, and red phosphorus - among other products (Cotton and Wilkinson, 1980). The boiling point of P_4O_6 is 175°C; it is a colorless liquid at room temperature. The hydrolysis reaction can be considered to be diffusion-limited.

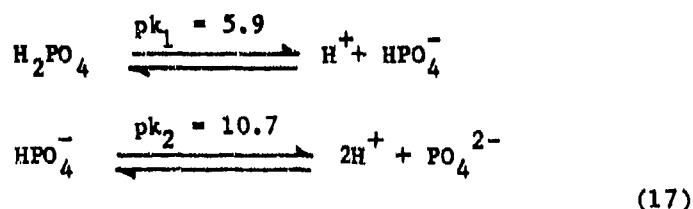
d. Phosphoric Acid (H_3PO_4)

Phosphoric acid (also called orthophosphoric acid) is produced when phosphorus pentoxide is exhaustively hydrolyzed. Phosphoric acid

is very inert. Significant reactions are dehydration to pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) and reduction by metals. These reactions have a significant rate only at elevated temperatures. The acid is tribasic and the following ionizations (equation 16) are known to occur (Cotton and Wilkinson, 1980).



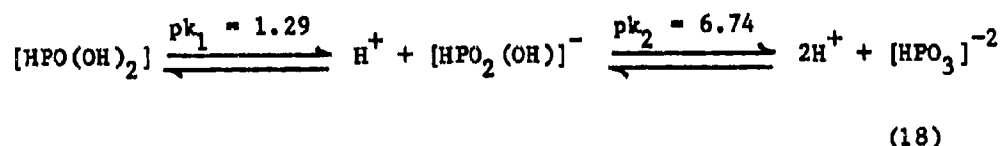
The UV-VIS spectra of phosphoric acid has been reported (Fox, 1970). The spectrum is pH-dependent. HPO_4^{2-} has two extremely weak internal transitions above 200 nm and a medium-intensity charge-transfer-to-solvent (CTTS) band below 200 nm. H_2PO_4^- has only the medium-intensity CTTS band below 200 nm. Photolysis of either anion below 200 nm leads to a hydrated electron and the appropriate radical. The following equilibria have been established (Huber and Hayon, 1968):



A quantum yield of 0.506 has been reported for the photolysis of HPO_4^{2-} (Halmann and Platzner, 1961). However, the solar flux below 200 nm is very small and these photolysis reactions are not expected to be environmentally important.

e. Phosphorus Acid (H_3PO_3)

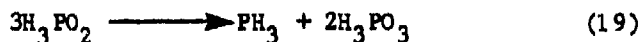
Two formulations of H_3PO_3 stoichiometry were found in the literature: $[\text{HPO}(\text{OH})_2]$ and $[\text{P}(\text{OH})_3]$. The first of these two, as shown in equation 18, is the best.



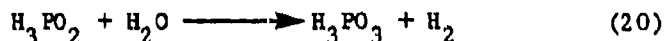
Phosphorus acid is dibasic. It decomposes thermally to give phosphoric acid, hydrogen, phosphine, and red phosphorus--along with many lower and condensed oxyacids. The oxidation of phosphorus acid to phosphoric acid is slow and very complicated. Preliminary results indicate a chain mechanism (Van Wazer, 1958).

f. Hypophosphorus Acid (H_3PO_2)

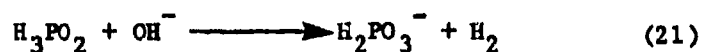
Hypophosphorus acid, like phosphorus acid, has two possible tautomers: $[\text{H}_2\text{PO}(\text{OH})]$ and $[\text{HP}(\text{OH})_2]$. Unlike phosphorus acid, an equilibrium constant for the tautomerization ($K = [\text{H}_2\text{PO}(\text{OH})]/[\text{HP}(\text{OH})_2]$) has been reported to be 10^{-12} at 25° . This has been estimated from reaction data, although the $[\text{HP}(\text{OH})_2]$ form has not been observed. Thermal disproportionation is important:



As with phosphorus acid, this is not a clean decomposition but gives many other products. Hypophosphorus acid is hydrolyzed according to equation (20):



A rate constant of $3 \times 10^{-4} \text{ min}^{-1}$ at 100°C has been quoted for the reaction with base:



Metal ions also catalyze the hydrolysis reaction. In addition, oxidation is an important reaction of H_3PO_2 , with the conversion between forms of H_3PO_2 being rate-determining.

g. Phosphine (PH_3)

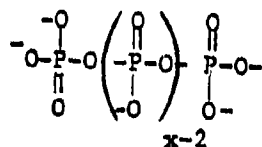
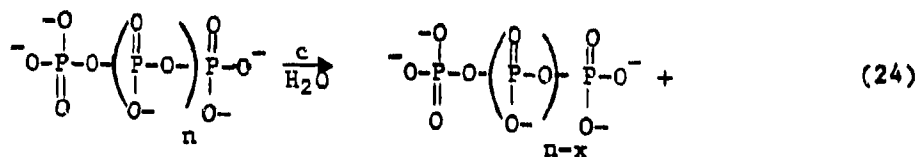
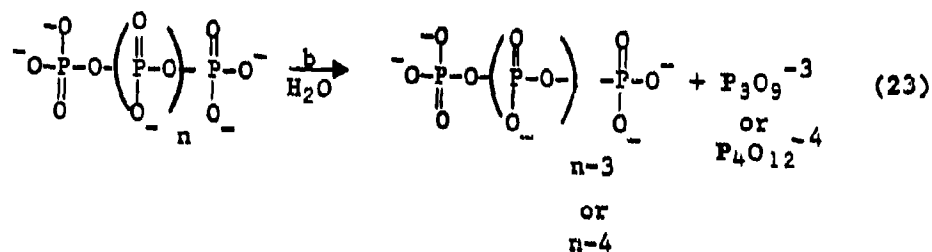
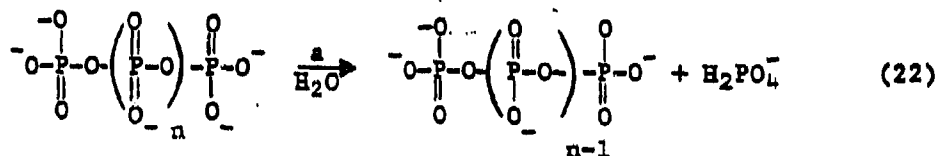
Phosphine will be produced in any phosphorus oxidation with less than stoichiometric quantities of oxygen in the presence of water (Flock, 1973). Phosphine is a gas that is sparingly soluble in water. Thus, it is expected to be found in the vapors above phosphy waters and perhaps in the munitions smokes. It does not spontaneously ignite in air. The oxidation of phosphine, like the other phosphorus compounds reported here, follows a branching-chain mechanism. This means that upper and lower critical pressures of oxygen pressure exist; in this case, the reaction is explosive between these limits and very slow outside of them. However, this upper limit for oxygen is around 100 mm Hg partial pressure over a wide range of phosphine partial pressures. Because the partial pressure of oxygen in the atmosphere is normally above this, an explosive mixture will be formed only at very high phosphine pressures. The result is that until the phosphine concentration is quite high, the reaction goes by the slow pathway, which means that it has a reasonable lifetime. Van Wazer (1958) describes the reaction in this region as no reaction unless the reaction is initiated by a flare or by UV irradiation. The photolysis of phosphine and the oxidation after initiation by photolysis have been studied by Norrish and Oldershaw (1961a, 1961b).

The absorption spectra of gaseous PH_3 has a band structure in the region above 225 nm (236, 232, 229, and 228 nm) and a continuous band between 225 and 185 nm. The quantum yield for hydrogen formation on

photolysis above 200 nm is about 0.56. Photolysis below 200 nm leads to PE in both the Π and ${}^3\Sigma$ states (Calvert and Pitta, 1966).

h. Linear Polyoxoacids

The polyoxoacids are all nonvolatile, water-soluble liquids or solids. The primary chemical reaction of concern is hydrolysis. For acids containing four or more phosphate groups, three pathways of hydrolysis are available; a) end group-clipping, b) cyclic phosphate abstraction, and c) random cleavage, as shown in equations 22, 23, and 24, respectively.

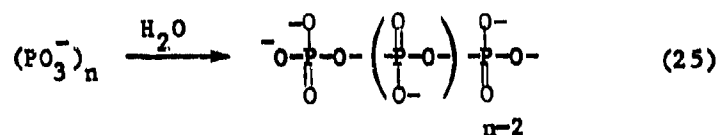


The distribution between these pathways is very pH-dependent. At very low pH values, the hydrolysis pathway is $c > a > b$; in the pH range of 3 to 7, the pathway is $a > b > c$; at pH between 8 and 10, the

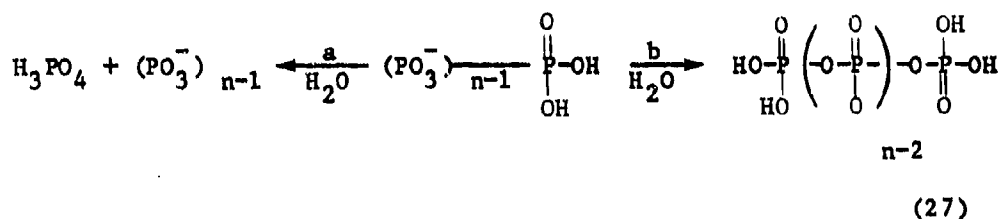
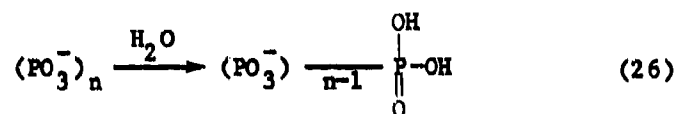
pathway is $a \sim b > c$; and above pH 10, the ratios of a and b are roughly equal, with no contribution from pathway c. At neutral pH, the rate constant (first-order in $[\text{PO}_3^-]$) is 4.9×10^{-4} for b, 1.7×10^{-4} for c, and $1.34 \times 10^{-3} \text{hr}^{-1}$ overall. The hydrolysis can also be catalyzed by metal ions (Osterheld, 1972); however no data were reported by which we could estimate the impact of metal ions in the hydrolysis rate constant.

1. Cyclic Polyphosphates

Hydrolysis of cyclic polyphosphates closely follows that of the linear phosphates. However, two first steps are possible: one is the opening of the ring to give the linear polyphosphate (equation 25):



which then decomposes by the mechanisms discussed above. Another step is the degradation of the ring to the next lower cyclic polyphosphate and one end group (equation 26):



This product can decompose by two pathways; a) end-group cleavage or b) opening of ring to give the straight chain (equation 27). The overall rate is highly pH-dependent. At neutral pH, the reported

first-order decomposition rate has been reported to be $2.2 \times 10^{-5} \text{hr}^{-1}$ (Osterheld, 1972).

C. Biotransformation

1. White Phosphorus

Little is known about the biological transformation of white phosphorus. Under aerobic conditions, biotransformation would be minimal due to the rapid chemical transformation of white phosphorus and dissolved oxygen. This reaction would tend to create anaerobic environments where biotransformation could occur slowly. However, no data are available on anaerobic processes.

White phosphorus has been tested as a phosphate fertilizer (Rodrigues et al., 1972; Bohn et al., 1970). In neutral, calcareous, and limed soil, white phosphorus is quickly oxidized to phosphate and is effectively used by plants. In acid soil, the process was slow and phosphate was not available for plants for a month or more. The biological processes under such conditions are not clear.

2. Red Phosphorus

Red phosphorus is chemically less active than white phosphorus, and therefore is more persistent in soil or water. Little information is available on the biotransformation of this chemical.

Red phosphorus has been tested as a phosphate fertilizer (Sokolov et al., 1976; Jackman et al., 1970). It has a long residual activity and its efficacy as a fertilizer depends on the rate of its oxidation in soil. The role that microbes play in its oxidative transformation is unknown.

3. Phosphorus Oxides

In soil or water, phosphorus oxides undergo hydrolysis to produce oxyacids. Because microorganisms cannot use the oxides without the

presence of moisture, we expect that biotransformation will not be an important fate process.

4. Hypophosphorous Acid

Heinen and Lauwers (1974) conducted growth experiments with three different phosphorus sources and showed that Bacillus caldolyticus can utilize phosphite and hypophosphite just as well as phosphate. Hypophosphite was very quickly oxidized to phosphate and accumulated in the medium.

Therefore, hypophosphite may be biotransformed in soil and water by microorganisms. However, no data on its biotransformation rate are available.

5. Phosphorus Acid

The biological oxidation of phosphite was first demonstrated by Adams and Conrad (1953). They observed that phosphite added to soil samples disappeared, with a corresponding increase in phosphate concentration. The oxidation of phosphite proceeded only when microbial activity was not restricted by the presence of a bactericidal agent such as toluene.

Casida (1960) investigated the ability of a number of microbial cultures to utilize phosphite during heterotrophic growth. Several organisms were found to utilize phosphite, and one of the bacteria--Pseudomonas fluorescens--converted phosphite to orthophosphate, which accumulated in the growth medium. Malacinski and Konetzka (1966) confirmed that several species of organisms can use phosphite as a sole phosphorus source, and P. fluorescens utilized phosphite as efficiently as phosphate. The ability of P. fluorescens to oxidize phosphite was shown to be inducible, and a period of adaptation was required. Later, Malacinski and Konetzka (1967) purified a phosphite oxidase from P. fluorescens. In B. caldolyticus, Heinen and Lauwers (1974) reported that this organism could utilize phosphorus as phosphate, phosphite, or hypophosphite.

The reduction of phosphite to hypophosphite was reported by Tsubota (1959). He showed that phosphite and hypophosphite were formed in rice paddies and isolated anaerobic bacteria, which catalyzed these reactions. He also showed that Escherichia coli and Clostridium butyricum (common laboratory strains) can reduce PO_4^{-3} to PO_3^{-3} and further reduce it to PO_2^{-3} .

The half life of phosphite oxidation in San Joaquin clay loam soil was 12 to 16 weeks (Adams and Conrad, 1953); when starch was added to the same soil, the half life was 8 to 12 weeks. No other rate data were given. The transformation may vary with the availability of soluble phosphate, organic content, or other nutrients of the soil.

6. Phosphoric Acid

Phosphorus occurs in living organisms and soils only in the +5 valence state--either as free phosphate ions or as organic phosphate constituents of the cells. Phosphates in the cells are presented as major cell components (e.g., DNA, RNA, lipidphosphate), fundamental metabolic compounds (e.g., hexose phosphates, nucleotides), and energy transport compounds (e.g., ATP, DPN), and they play an important role in the life process.

In contrast with nitrogen and sulfur, plants and most of the microorganisms do not reduce phosphate. Rudakov (1929) observed the reduction of mineral phosphates in soil under anaerobic conditions. Different soil types were found to vary in their capacity to bring about the reduction of phosphate, and pure cultures of phosphate-reducing microorganisms were isolated from the soil samples. Tsubota (1959) reported that phosphate reduction took place in flooded rice-paddy fields and isolated anaerobic bacteria catalyzing these reactions. Phosphite and hypophosphite were identified by paper chromatography. He also showed that such common laboratory strains as E. coli and C. butyricum can reduce phosphate to phosphite and further to hypophosphite.

There is no confirmed evidence that the most reduced state of phosphate reduction, phosphine, is produced (Burford and Bremner, 1972) although Tsubota (1959) reported the evolution of phosphine. However, he also showed that phosphine is sorbed by soil constituents and may not be released to the atmosphere if produced in soils.

The information on the biological reduction of phosphate is not sufficient to assess its importance in the fate of phosphate in the environment.

Soil phosphate is most conveniently divided into two categories--insoluble phosphate and readily soluble phosphate. The insoluble phosphate, which is not directly available to plants or microorganisms, usually constitutes about 95 to 99% of the total soil phosphate in the environment. Total phosphate in soils ranges from 130 to 1600 ppm. Because only a small fraction of phosphorus is available for plants, phosphorous fertilizer is required for agricultural crops. Microorganisms can solubilize some insoluble phosphates to soluble phosphate by the excretion of organic and inorganic acids, carbon dioxide, or hydrogen sulfide. Furthermore, microorganisms can immobilize soluble phosphate through the incorporation of soluble phosphate into growing cells (1.5 to 2.5% of dry weight).

The role of microorganisms in transformation of phosphate is mainly concerned with solubilization and immobilization of the phosphate, and perhaps less with reduction of phosphate. The processes are affected by pH and by the presence of organic materials, other minerals, etc., in soils and waters. Because of the relatively high content of insoluble phosphate in soils and because phosphate is an important mineral nutrient of plants, the accumulation of phosphate in cultivated soils should be beneficial rather than polluting (Hayman, 1975; Alexander, 1977).

7. Polyphosphates

Karl-Kroupa et al (1959) reported that cell suspensions of bacteria Escherichia coli, the fungus allomyces, and higher plant species can enzymatically accelerate the hydrolysis reaction of tripolyphosphate. With 40×10^{-3} mg/l of E. coli cells (dry weight), the half-life of tripolyphosphate was 20 hrs after 65 hrs of lag time compared to half-life of more than 10,000 hrs in control water. Sutton and Larsen (1963) added sodium pyrophosphate solutions to a wide variety of soils and determined the rate of hydrolysis to orthophosphate. They found that hydrolysis rate is correlated to the soil biological activity as measured by rate of CO_2 evolution. The half-lives of pyrophosphate were found to range from 4 days to 100 days. Gilliam and Sample (1967) also showed that the hydrolysis of pyrophosphate was much faster in the non sterile soils than in autoclaved soils. From the above studies, it appears that polyphosphates will be biologically hydrolyzed and the processes will be faster than chemical hydrolysis. However, these reports did not provide enough information to determine biotransformation or indicate the ability of microorganisms to hydrolyze higher polyphosphate homologs.

8. Phosphine

Phosphine is a gas at ambient temperatures; hence most of the phosphine is probably transported to the atmosphere. However, Burford and Bremner (1972) showed that soils could sorb phosphine, which therefore could be acted upon by microorganisms. No transformation data on this compound have been reported.

9. Butyl Rubber and Felt

Felt is a pure form of cellulose. Cellulolytic microorganisms are common in field and forest soils and can be found in decaying plant tissues. Many fungi and bacteria utilize cellulose as a carbon and energy source (Alexander, 1977). The transformation of cellulose

is affected by temperature, pH, aeration, moisture, and available nitrogen, and other organic nutrients. However, no transformation rate data on felt are available.

Raw unvulcanized and vulcanized butyl rubber can be transformed by soil and water microorganisms (Zyska, 1981). The biotransformation in the environment can be affected by the presence of polymer compounding ingredients, the shape of the butyl rubber, and the related environmental factors mentioned for felt. However, no rate data on this particular rubber formulation were found.

10. Biouptake

Agricultural crops contain 0.05 to 0.50% phosphorus in their tissues (Alexander, 1977). About 2-11 kg/half acre/year of phosphorus is taken up by crops and trees (Hayman, 1975). If the plant compost remains on the land, phosphorus will be released by microorganisms and returned to the uptake cycle.

Other phosphorus compounds with lower oxidation states could not be taken up by plants (Doby, 1965; MacIntire et al., 1950). Although white and red phosphorus have been tested as fertilizers, they are oxidized in the soil before being assimilated by plants (Bohn et al., 1970; Sokolov et al., 1976).

11. Biosorption

Using the correlation equation relating K_{oc} with K_B , as described by Baughman and Paris (1981),

$$K_B = 0.16 K_{oc} \quad (28)$$

K_B is estimated to be approximately 1800 for white phosphorus.

No information about microbial sorption of other phosphorous compounds is available. Phosphate will be taken up by microbial cells and metabolized rather than being absorbed (1.5-2.5% of cells). The metabolized phosphate will be returned to the ecosystem when the cell dies.

12. Bioaccumulation

The ability of white phosphorus to accumulate in the tissue of aquatic organisms has been the subject of extensive investigation, particularly with regard to uptake by marine life. The data have been tabulated and reviewed by Sullivan et al. (1979). White phosphorus rapidly becomes concentrated to levels 20 to 100 times above ambient concentrations in the tissues of aquatic organisms, or up to several thousand times in codliver tissue. However, this effect does not represent a bioaccumulation in the sense that pesticide residues permanently lodge in tissue. White phosphorus remains mobile; consequently, its concentration rapidly decreases after transfer of a contaminated organism to clear water.

Phosphorus is an important nutrient of all living life. It is taken up through food and metabolized. It will be released to the environment when the animal dies and the cell is decomposed by microorganisms. No information on bioaccumulation of other phosphorus compounds is available.

VI. CONCLUSIONS AND RECOMMENDATIONS FOR PHASE II SCREENING TESTS

The literature review revealed a paucity of data relevant to the estimation of persistence of phosphorus and its transformation products under environmental conditions. To identify the gaps in the literature, a matrix was constructed of chemicals expected to be derived from phosphorus manufacturing and deployment and the physical properties and processes for which data are required (Table 2). The matrix is shown in Table 4.

Very few rate constants necessary for an environmental fate assessment have been reported in the literature. Oxidation will be an extremely important process for white and red phosphorus in all environments, and hydrolysis reactions will dominate the transformation of phosphorus oxides in the presence of moisture. To estimate the importance of these processes relative to processes such as photolysis, reduction, and biotransformation, we recommend that transformation screening studies be performed as described in our proposal (Smith et al., 1982).

The investigations should begin with solubility and vapor pressure measurements. From these data, estimates of the partition coefficients and Henry's constants can be calculated. The latter data will aid in the estimation of the magnitude of volatilization rate constants.

Leachability studies should be initiated in PBA soils. Based on the motility of phosphorus and its transformation products, the need for studies on diffusion and dissolution rate will be evaluated.

The magnitude of the transformation rate constants (especially oxidation and hydrolysis) needs to be established for all environments. Reduction may not be a significant fate process and possibly

can be eliminated from detailed study, depending on the results of screening studies

The ultraviolet-visible absorption spectrum should be measured for all compounds. Those compounds absorbing in the solar spectral region (> 290 nm) should then be screened for photochemical reactivity and their quantum yields should be determined.

Biotransformation is not considered to have a major impact on the transformation of phosphorus, especially in aerobic environments. However, screening studies should be performed in anaerobic environments, where reductive processes may become important.

Essentially no environmental data on physical properties or transformation rates are available for red phosphorus. Although this compound is expected to behave in a similar fashion to white phosphorus, particular attention should be devoted to the establishment of a property/process data base for red phosphorus.

TABLE 4. MATRIX PROFILE OF PROCESSES/PROPERTIES
THAT NEED TO BE EVALUATED FOR A FATE ASSESSMENT

	White Phosphorus	Red Phosphorus	P ₄ O ₆ Phosphorus Tetraoxide	P ₄ O ₃ Phosphorus Trioxide	H ₃ PO ₂ Hypo- phosphorus Acid	H ₃ PO ₃ Phosphorus Acid	P ₂ -P ₄ Poly phosphoric Acids	P ₂ ,P ₄ ,P ₆ Meta Phosphates Cycle	Phosphine	H ₃ PO ₄ Phosphoric Acid
Solubility, mg l ⁻¹	3		DEC	DEC		3 x 10 ⁴	DEC	DEC		5.5 x 10 ⁴
Vapor Pressure, torr	.04 25°C		NH	NH	NH	NH	NH		2700	NH
Evaporation Rate	Soil Water									
Adsorption Partition Coefficient, K _d	77		A	A						
Octanol/Water Partition Coefficient, K _{ow}	4.2 - 4.9		A	A	A	A	A	A		A
Leachability			A	A						
Henry's Constant, H Torr liter mole ⁻¹	400									
Particle Deposition Rate										
Dissolution Rate										
Diffusion Rate										
Hydrolysis Rate	Air	A	A	A						A
	Soil	A	A	A						A
	Water	.07 to .007 hr ⁻¹	A				4.9 x 10 ⁻⁴ hr ⁻¹	1.3 x 10 ⁻⁴ hr ⁻¹		A
Oxidation Rate	Air	B	A	A			A	A		A
	Soil	B	A	A			A	A		A
	Water	.8 to .03 hr ⁻¹	DEC	DEC			A	A		A
Reduction	Air	A	A	A	A	A	A	A	A	A
	Soil	A	A	A	A	A	A	A	A	A
	Water	A	A	DEC	DEC	A	A	A	A	A
Absorption Spectrum									185 - 225 nm	>200 nm
Photochemical Rate	Air	A	A	A						A
	Soil	A	A	A						
	Water	A	A	DEC	DEC					
Quantum Yield									.5	.6
Anaerobic Biotransforma- tion Rate	Soil	A	A	A			A	A		A
	Water	A	A	DEC	DEC		A	A		A
	Soil									
Anaerobic	Water			DEC	DEC					
Bioconcentration, K _b	1000		A	A	A	A	A	A		A
Bioaccumulation	20-100		DEC	DEC						NH
Biouptake			DEC	DEC						NH

A = Soluble
B = Diffusion Controlled
NH = Not Necessary
DEC = Decomposes

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